The Experimental (Calorimetric and Visual) Investigation of Phase Transitions in the "Water – n-Hexane" Binary System

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The liquid–liquid and liquid–gas phase transitions including critical states are investigated in the "water – n-hexane" system with the aid of a high-temperature adiabatic calorimeter where the isochoric heat capacity $C_{v,x}$ was measured. The phase transition is identified itself by the jump of $C_{v,x}$, which can be accurately observed. Measurements were made of $C_{v,x}$ for the mixtures with 0.028, 0.045, 0.0643, 0.0673, 0.0981, 0.25, 0.50, 0.55, 0.58, 0.60, 0.61, 0.75, and 0.90 weight fractions of water along isochores. We have noticed two jumps in the heat capacity, characterizing the liquid–liquid and liquid–gas phase transitions.

The phase transitions are identified experimentally with the aid of an optical cell. The experiment was carried out at three different compositions: 0.045, 0.50 and 0.80 weight fractions of water at temperatures from 300 – 500 K and at pressures up to 6.5 MPa.

The investigations allowed as to trace the "P-T" and "T-x" phase diagrams. The lower branch of the line of the critical points starts from the critical point of the more volatile component and finishes at the UCEP, which has a composition of 0.0673 weight fraction of water. The upper branch of the line of critical points starts at the critical point of water. When the concentration of n-hexane increases, the critical temperature begins to decrease, then passes a minimum at the composition with 0.75 weight fraction of water and rises deeply up to the composition with ≈ 0.62 weight fraction of water. In the interval of the compositions with 0.0673 ÷ 0.62 weight fractions of water, "liquid – gas" critical phenomena have not been observed.

For the composition appropriate to the critical endpoint the expected the behavior of $C_{v,x}$ is observed. For the other compositions along isochores, renormalization of the critical index α take place. The dependence of $C_{v,x}$ on the temperature is described by a power law with $\alpha = 0.11$ for the phase transition in the region where $dT_c/dx \approx 0$. In the area where the critical liquid-gas phenomena are not realized, the behavior of $C_{v,x}$ has a special character. Near the point of maximum temperature it has the form of parabola. The jump of heat capacity is absent.

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